

**Zh.G. Bazarova^{1,2}, V.G. Grossman¹, B.G. Bazarov^{1,2},
Yu.L. Tushinova^{1,2}, O.D. Chimitova¹, Ts.T. Bazarova¹**

¹*Baikal Institute of Nature Management,
Siberian Branch of Russian Academy of Sciences,
8 Sakhyanovoi St., Ulan-Ude, 670047, Russian Federation*

²*Buryat State University,
24a SmolinaSt., Ulan-Ude, 670000, Russian Federation
e-mail: jbaz@binm.ru*

Phase diagrams for the $M_2MoO_4-Ln_2(MoO_4)_3-Hf(MoO_4)_2$ systems, where $M = Li-Cs$, Tl and $Ln = La-Lu$

In this paper, the results of systematic studies of complex molybdate systems $M_2MoO_4-Ln_2(MoO_4)_3-Hf(MoO_4)_2$ ($M = Li-Cs, Tl$; $Ln = La-Lu$) are presented. Subsolidus phase diagrams of ternary systems were constructed and new triple molybdates were obtained. The optimum synthesis conditions for poly- and monocrystalline form were determined. According to single-crystal data, the structure of one of the representatives of triple molybdates was determined.

Keywords: phase equilibria, synthesis, systems, lithium, sodium, potassium, rubidium, cesium, thallium, lanthanides, hafnium, crystal structure.

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Introduction

The molybdates containing tetrahedrally coordinated anions MoO_4^{2-} are among the most exciting objects in inorganic and crystal chemistry. Special attention has been paid to the molybdates that include luminescent elements, such as Ce, Pr, Eu, Tb, Tm, in their composition. These compounds can be used as phosphors for white light emitting diodes. Currently, numerous studies had been undertaken that aim to search for new effective phosphors for the creation of

WLED. These phosphors should possess high stability, compactness, high luminescence efficiency when excited by near UV, long lifetime and low cost. Luminescent materials containing rare-earth elements are also within the scope of such studies [1–3]. In this paper, we present results on the study of phase equilibria in ternary molybdate systems containing single-, three- and tetravalent elements, as well as data on the crystal structure of complex molybdate structural types.

Experimental

Reagents Li_2MoO_4 (“pure” grade), $Na_2MoO_4 \cdot 2H_2O$ (“pure for analysis” grade), K_2MoO_4 (“pure” grade), Cs_2MoO_4 (“pure” grade), Rb_2CO_3 (“chemi-

cally pure” grade), Tl_2O_3 (“chemically pure” grade), MoO_3 (“chemically pure” grade), HfO_2 (“chemically pure” grade), and rare earth oxides of 99.9% purity

were used as starting materials. $\text{Hf}(\text{MoO}_4)_2$ and $\text{Ln}_2(\text{MoO}_4)_3$ were synthesized by the solid state method. The annealing had started at 400–500 °C with the following temperature increase up to 800 °C in order to prevent MoO_3 losses due to its high volatility. The total calcination time was 100–150 h. Rb_2MoO_4 was prepared within the temperature range 350–650 °C during 100 h. Tl_2MoO_4 was synthesized during 50 h firing starting at 400 °C with final temperature equal to 550 °C. The samples were regrinded after each 24 h in the course of annealing in order to reach better homogeneity.

Results and discussion

The data concerning phase equilibrium for the side systems of studied triangles (quasi-ternary systems) M_2MoO_4 – $\text{Ln}_2(\text{MoO}_4)_3$ – $\text{Hf}(\text{MoO}_4)_2$ ($\text{M} = \text{Li}$ – Cs , Tl ; $\text{Ln} = \text{La}$ – Lu) are taken from the literature. The phase formation in the quasi-binary Li_2MoO_4 – $\text{Ln}_2(\text{MoO}_4)_3$ systems was described in paper [4] in details. The aforementioned systems can be divided into two groups. The first group includes systems with $\text{Ln} = \text{La}$ – Tb in which two intermediate phases $\text{LiLn}_5(\text{MoO}_4)_8$ and $\text{LiLn}(\text{MoO}_4)_2$ possess a significant homogeneity range. The second group includes the systems with $\text{Ln} = \text{Dy}$ – Lu . Inside these systems two intermediate compounds that did not exhibit any noticeable homogeneity ranges were detected: $\text{LiLn}(\text{MoO}_4)_2$ and $\text{Li}_7\text{Ln}_3(\text{MoO}_4)_8$.

Two intermediate compounds with the constituents mole ratio of 5:1 and 1:1 were detected inside the quasi-binary Na_2MoO_4 – $\text{Er}_2(\text{MoO}_4)_3$ systems similarly to the K_2MoO_4 – $\text{Ln}_2(\text{MoO}_4)_3$ ($\text{Ln} = \text{La}$, Tb , Dy , Er), M_2MoO_4 – $\text{Ln}_2(\text{MoO}_4)_3$ ($\text{M} = \text{Tl}$, Rb ; $\text{Ln} = \text{La}$ – Lu) systems [4–8]. Additionally to those two one more intermediate

The phase formation inside a sub-solidus region of the ternary salt systems M_2MoO_4 – $\text{Ln}_2(\text{MoO}_4)_3$ – $\text{Hf}(\text{MoO}_4)_2$ ($\text{M} = \text{Li}$ – Cs , Tl ; $\text{Ln} = \text{La}$ – Lu) in air were studied using the intersecting joins method. The phase composition of the samples was monitored by X-ray diffraction (XRD) measurements using Bruker D8 Advance diffractometer (Cu K α radiation, VANTEC-1, maximum angle $2\theta=100^\circ$, scan step 0.01–0.02°). Primary fitting of the diffraction patterns was made using PROFAN software from the CSD package.

phase with the constituents mole ratio 1:5 was found to exist inside the Na_2MoO_4 – $\text{Ln}_2(\text{MoO}_4)_3$ ($\text{Ln} = \text{Nd}$, Sm) and K_2MoO_4 – $\text{Sm}_2(\text{MoO}_4)_3$ systems [4, 5].

The phases formed inside the cesium-containing rare-earth molybdate systems included those with the constituents mole ratio 3:1 and 1:1 with $\text{Ln} = \text{Nd}$, whereas the systems with $\text{Ln} = \text{Sm}$, Tb , Er revealed only 1:1 compound [4, 5].

Lithium hafnium molybdate with the significant homogeneity range $\text{Li}_{10-4x}\text{Hf}_{2+x}(\text{MoO}_4)_9$ ($0.21 \leq x \leq 0.68$) was formed in the Li_2MoO_4 – $\text{Hf}(\text{MoO}_4)_2$ system [9], but in the oxide systems with larger alkali earth metals M_2MoO_4 – $\text{Hf}(\text{MoO}_4)_2$ ($\text{M} = \text{K}$, Tl , Rb , Cs) two types of compounds were confirmed – $\text{M}_8\text{Hf}(\text{MoO}_4)_6$ and $\text{M}_2\text{Hf}(\text{MoO}_4)_3$ [10–13]. It should be noted that Na-containing system slightly differs from the aforementioned ones. It was found that along with phases with the constituents mole ratios equal to 4:1 and 1:1 one more compound is formed with the 3:1 composition.

The phases that were isolated in the $\text{Ln}_2(\text{MoO}_4)_3$ – $\text{Hf}(\text{MoO}_4)_2$ systems

are $\text{Ln}_2\text{Hf}_3(\text{MoO}_4)_9$ ($\text{Ln} = \text{La-Tb}$), $\text{Ln}_2\text{Hf}_2(\text{MoO}_4)_7$ ($\text{Ln} = \text{Sm-Ho}$), and $\text{Ln}_2\text{Hf}(\text{MoO}_4)_5$ ($\text{Ln} = \text{Er-Lu}$) [14].

The phase diagrams for various molybdate systems are shown in Fig. 1–6, and the corresponding phase compositions are listed in Table 1.

No new compounds were detected in the lithium-containing and sodium-containing systems [15, 16]. In contrast, the new compounds listed in Table 1 and shown in Fig. 3–6 were confirmed in the $\text{M}_2\text{MoO}_4\text{-Ln}_2(\text{MoO}_4)_3\text{-Hf}(\text{MoO}_4)_2$ ($\text{M} = \text{K, Rb, Tl, Cs}$; $\text{Ln} = \text{La-Lu}$) systems [14, 17, 18].

The molybdates with the composition $\text{K}_5\text{LnHf}(\text{MoO}_4)_6$ were identified in the systems with $\text{Ln} = \text{Sm-Lu}$.

Two types of compounds, namely $\text{M}_5\text{LnHf}(\text{MoO}_4)_6$ (5:1:2) and $\text{M}_2\text{LnHf}_2(\text{MoO}_4)_{6.5}$ (2:1:4), were isolated in the $\text{Tl}_2\text{MoO}_4\text{-Ln}_2(\text{MoO}_4)_3\text{-Hf}(\text{MoO}_4)_2$ ($\text{Ln} = \text{Ce-Lu}$) and $\text{Rb}_2\text{MoO}_4\text{-Ln}_2(\text{MoO}_4)_3\text{-Hf}(\text{MoO}_4)_2$ ($\text{Ln} = \text{Ce-Lu}$) systems. In case of the Tl-containing systems, for $\text{Ln} = \text{Ce-Nd}$ one more phase except those mentioned above had been obtained – $\text{TlLnHf}_{0.5}(\text{MoO}_4)_3$ (1:1:1).

The phase with composition $\text{Cs}_2\text{LnHf}_2(\text{MoO}_4)_{6.5}$ (2:1:4) was found to

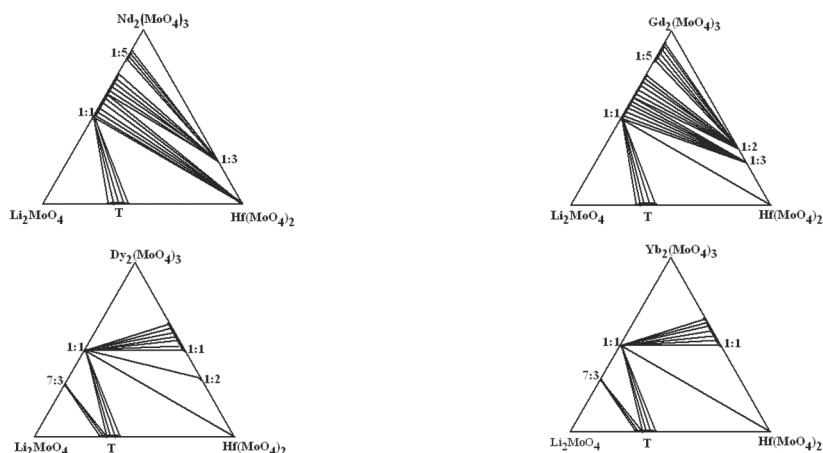


Fig. 1. Subsolidus phase diagrams of the $\text{Li}_2\text{MoO}_4\text{-Ln}_2(\text{MoO}_4)_3\text{-Hf}(\text{MoO}_4)_2$ systems ($\text{T} = \text{Li}_{10-4x}\text{Hf}_{2+x}(\text{MoO}_4)_9$, $0.21 \leq x \leq 0.68$; shaded double-phase equilibrium region) [15]

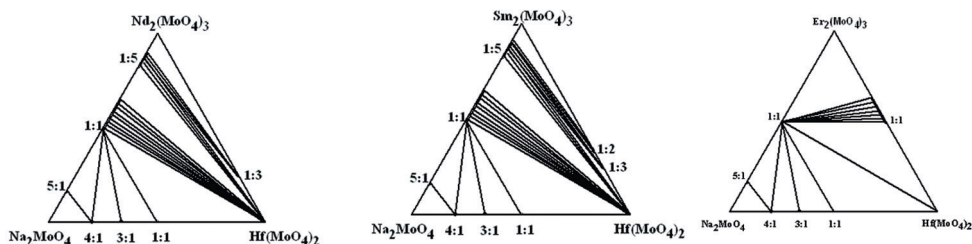


Fig. 2. Subsolidus phase diagrams of the $\text{Na}_2\text{MoO}_4\text{-Ln}_2(\text{MoO}_4)_3\text{-Hf}(\text{MoO}_4)_2$ systems; shaded double-phase equilibrium region [16]

exist in the Cs-containing rare earth molybdates with $\text{Ln} = \text{Pr} - \text{Lu}$.

The systems $\text{M}_2\text{MoO}_4 - \text{Ln}_2(\text{MoO}_4)_3 - \text{Hf}(\text{MoO}_4)_2$ ($\text{M} = \text{K}, \text{Rb}, \text{Tl}, \text{Cs}$; $\text{Ln} = \text{La} - \text{Lu}$) are characterized by the formation of a different number of phases with varying homogeneity ranges with respect to the lanthanide elements. One can see that $\text{M}_5\text{LnHf}(\text{MoO}_4)_6$ ($\text{M} = \text{K}, \text{Tl}, \text{Rb}$) compounds were formed if the size difference for the single charged M^+ cation and rare

earth element cation Ln^{3+} lies in the range of $0.682 \text{ \AA} \leq r(\text{M}^+)_{(\text{CN}=12)} - r(\text{Ln}^{3+})_{(\text{CN}=6)} \leq 0.859 \text{ \AA}$ [19]. In the case of $\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{Cs}^+$ such radii difference lies outside this range. As a result, formation of $\text{M}_5\text{LnHf}(\text{MoO}_4)_6$ compounds for these cations is impossible.

If the size difference for the single charged M^+ cation and rare earth element cation Ln^{3+} lies in the range $0.839 \text{ \AA} \leq r(\text{M}^+)_{(\text{CN}=12)} - r(\text{Ln}^{3+})_{(\text{CN}=6)} \leq 1.019 \text{ \AA}$, it

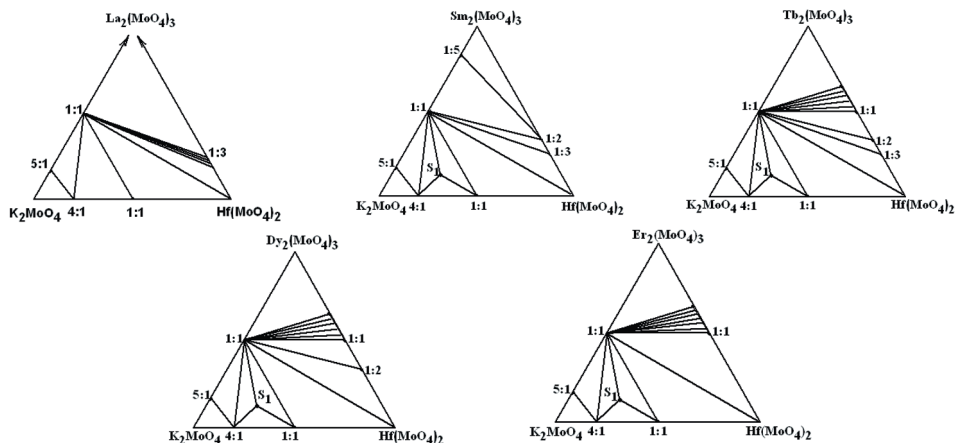


Fig. 3. Subsolidus phase relations in the $\text{K}_2\text{MoO}_4 - \text{Ln}_2(\text{MoO}_4)_3 - \text{Hf}(\text{MoO}_4)_2$ systems ($\text{S}_1 - \text{K}_5\text{LnHf}(\text{MoO}_4)_6$ (5:1:2); shaded double-phase equilibrium region) [14]

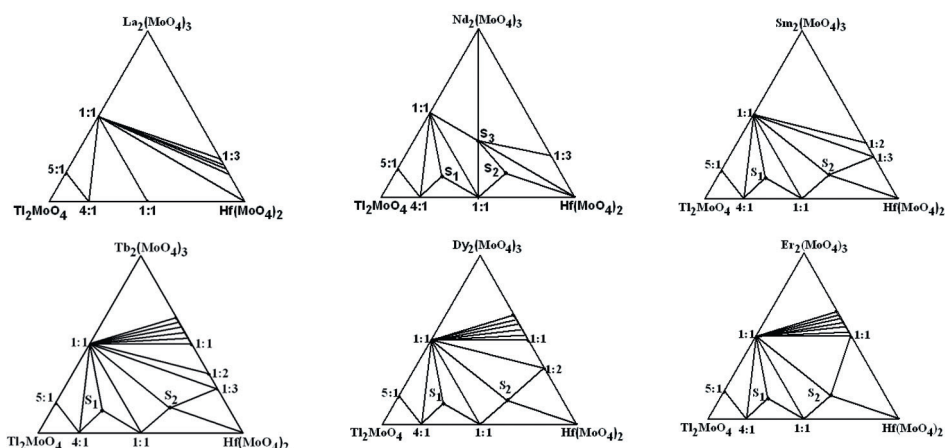


Fig. 4. Subsolidus phase diagrams for the $\text{Tl}_2\text{MoO}_4 - \text{Ln}_2(\text{MoO}_4)_3 - \text{Hf}(\text{MoO}_4)_2$ systems where $\text{Ln} = \text{La} - \text{Lu}$. Notations: $\text{S}_1 - \text{Tl}_5\text{LnHf}(\text{MoO}_4)_6$ (5:1:2), $\text{S}_2 - \text{Tl}_2\text{LnHf}(\text{MoO}_4)_{4.5}$ (2:1:4), and $\text{S}_3 - \text{TlLnHf}_{0.5}(\text{MoO}_4)_3$ (1:1:1); shaded double-phase equilibrium region [17]

Table 1

Compositions of triple molybdates in the M_2MoO_4 - $Ln_2(MoO_4)_3$ - $Hf(MoO_4)_2$
($M = Li-Cs$, Tl ; $Ln = La-Lu$) systems

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LiHf														
NaHf														
KHf					$K_3LnHf(MoO_4)_6$									
TlHf		$Tl_5LnHf(MoO_4)_6$												
		$Tl_2LnHf_2(MoO_4)_{6.5}$												
		$TlLnHf_{0.5}(MoO_4)_3$												
RbHf		$Rb_3LnHf(MoO_4)_6$												
		$Rb_2LnHf_2(MoO_4)_{6.5}$												
CsHf			$Cs_2LnHf(MoO_4)_{6.5}$											

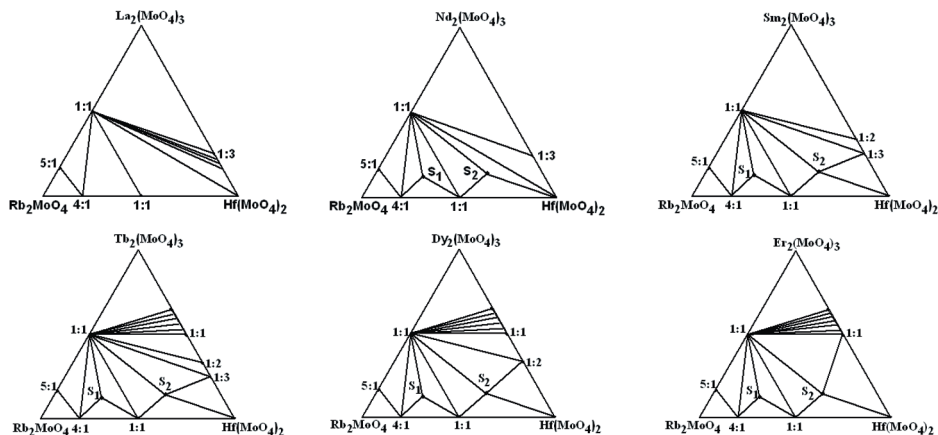


Fig. 5. Subsolidus phase diagrams for the Rb_2MoO_4 - $Ln_2(MoO_4)_3$ - $Hf(MoO_4)_2$ systems where $Ln = La-Lu$. Notations: S_1 - $Rb_5LnHf(MoO_4)_6$ (5:1:2) and S_2 - $Rb_2LnHf_2(MoO_4)_{6.5}$ (2:1:4); shaded double-phase equilibrium region [18]

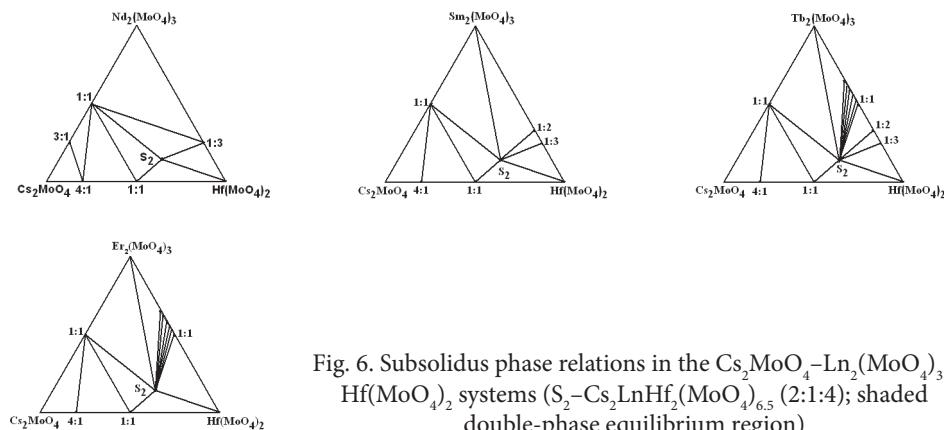


Fig. 6. Subsolidus phase relations in the Cs_2MoO_4 - $Ln_2(MoO_4)_3$ - $Hf(MoO_4)_2$ systems (S_2 - $Cs_2LnHf_2(MoO_4)_{6.5}$ (2:1:4); shaded double-phase equilibrium region)

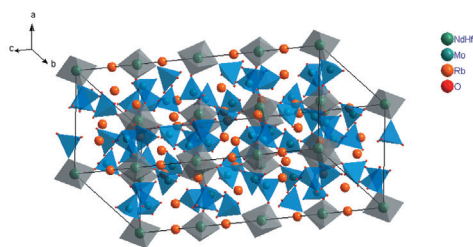


Fig. 7. Crystal structure fragment for $\text{Rb}_5\text{NdHf}(\text{MoO}_4)_6$

makes a formation of the $\text{M}_2\text{LnHf}_2(\text{MoO}_4)_{6.5}$ molybdates possible. The complex molybdates $\text{M}_5\text{LnHf}(\text{MoO}_4)_6$ ($\text{M} = \text{K}, \text{Tl}, \text{Rb}$) are isostructural to the earlier grown single crystals of $\text{Rb}_5\text{LnHf}(\text{MoO}_4)_6$ ($\text{Ln} = \text{Nd}, \text{Eu}, \text{Er}$), which possess the trigonal structure with $R\bar{3}c$ space group [18]. Three-dimensional framework of this

structure is built of the consequently alternating MoO_4 tetrahedra and $(\text{Ln}, \text{Hf})\text{O}_6$ octahedra linked with each other through the common O-vertices. One of the structural peculiarities for this class of compounds is a random distribution of Ln^{3+} and Hf^{4+} cations over two crystallographic sites with various distribution coefficients. Rubidium cations fill two types of large cavities in the framework, forming differently oriented channels of a large diameter. It gives good expectations for the fast ionic transport in such structures (Fig. 7).

Unfortunately, we have failed to prepare single crystals of $\text{M}_2\text{LnHf}_2(\text{MoO}_4)_{6.5}$ (2:1:4) and $\text{TlLnHf}_{0.5}(\text{MoO}_4)_3$ (1:1:1) in the condition used in the present work.

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